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Nanowire Probes for Magnetic Resonance Force Microscopy

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論文内容要旨

Magnetic resonance imaging (MRI) is well known as a powerful instrument for a visualizing three-dimensional structure inside a sample. However, the sensitivity and spatial resolution of the conventional MRI is limited by several tens to hundreds of micrometer scales due to limitations of conventional inductive detection techniques. In the early nineties, Magnetic resonance force microscopy (MRFM) combination with MRI and scanning probe microscopy (SPM) techniques is firstly invented by sidles, who also proposed the mechanical detection of a single spin. Comprehensive atomic-scale microscopy will exert a transformational impact in material science, nanoelectronics and microbiology. In order to realize the goal of single nuclear spin detection and atomic-scale resolution, great effort and persistence in theoretical and technical improvement are required. MRFM uses a high force-sensitivity probe with a magnetic tip to detect a force between a magnet and spins in the sample material while the spins are excited using magnetic resonance technique. A silicon nanowire probe is proposed that enable high force-sensitivity and response speed for MRFM application. The sensor, having shorter response time, is required because it takes much time from several tens of hours up to couple days for obtaining a three dimension image using current MRFM.

The first MRFM experiment demonstrating the MRFM principle is reported in 1992 (J.A. Sidle et al.), and involved the detection of electronic spin resonance (ESR) in diphenylpicrylhydrazil (DPPH). Shortly thereafter, two DPPH particles were successfully imaged in 1993 (O. Züger et al.). The next step involved transferring the expertise gained in the ESR experiments to the detection of nuclear magnetic spins. As the "magnetic moment of common nuclei are at least 650 times smaller than the moment of the electron", the detection of nuclear spins is, in general, more difficult. Nonetheless, detection of nuclear magnetic resonance (NMR) via the MRFM principle is successfully performed. Paralleling the development of the ESR experiments, imaging of nuclear spins is later carried out. Obtained in a span of several years in the early 1990s, these results were all positive and reinforced the feasibility of single spin detection Motivation of electron or nuclear spins. In order to achieve single spin detection, the focus returned to electron spins. An improvement in the detectability of several orders of magnitude required countless improvements, among which is the fabrication of better cantilevers, a better understanding of the inversion and nutation of the electron spins, and spin relaxation effects.

Recently, researchers succeeded in detecting a single electron spin, two-dimensional imaging of nuclear spins with a spatial resolution of 90 nm and three-dimensional images of individual tobacco mosaic viruses with a resolution better than 10 nm using MRFM technique. The last result, compared to conventional magnetic resonance detection methods that use inductive coils to sense nuclear spins, MRFM is about 100 million times more sensitive. However, reaching the ultimate goal of single-molecule imaging will require innovations that radically enhance the technique's sensitivity.

The basic idea behind MRFM is to sense the nuclear or electron spins in a sample by measuring the force that a magnetic field gradient exerts on these moments. Usually, this is achieved by having the magnetic force drive a small mechanical oscillator, such as a microfabricated cantilever. As a force detector, micro- and nanocantilevers are of great interest for a number of applications, such as magnetometry of nanoscale magnetic particles, femtojoule calorimetry, and various types of force microscopy. In particular, the proposed detection of single-spin magnetic resonance using MRFM requires the detection of forces in an attonewton (1 aN=10^{-18} N) range, which is much smaller than typical resolution of scanning force microscopy, i.e. approximately piconewton. Recent advances in fabrication of micro- and nanoelectromechanical systems (MEMS/NEMS) have allowed researchers to detect extremely small masses, forces, and displacements using a resonant sensor. Nanomechanical structures of a nanowire and nanotube have been proposed for next-generation mass and force sensors because of their small size and excellent material properties. In particular, silicon nanowires have been widely studied as a promising candidate in mass and force detection. In general, two techniques have been developed for fabrication of silicon nanowires such as bottom-up approach (Vapor liquid solid (VLS), oxide assisted growth (OAG), and metal assisted chemical etching and top-down approach. The bottom-up method is a growth or synthesized technique of the silicon nanowires from bulk silicon wafer either metal catalyzed-assisted or metal catalyzed-free. Meanwhile, top-down approach starts from bulk silicon wafer and scales down to the desired size and shape of silicon nanowires using a lithographic process. Generally, the fabrication of silicon nanowires via a top-down process which employed the application of advanced nanolithography tools on silicon-on insulator (SOI) is mostly compatible with conversional complementary metal oxide-semiconductor (CMOS) or nanomechanical resonator technology that typically consist of deposition, etching and patterning steps. Basically, the silicon nanowires fabrication started from the bulk material and scaled down into a single silicon nanowire or silicon nanowire array that can be formed with the help of nanolithography techniques such as electron-beam lithography (EBL), lithography patterned nanowires electro deposition, nano imprint lithography, and photolithography.

The purpose of this thesis is to develop a high force sensitive probe to detect attonewton force for MRFM at room temperature. In order to minimize the minimum detectable force of the silicon nanowire probe, a design model considering the geometry and fabrication of silicon nanowire having detectable force of attonewton-scale at room temperature, integration of silicon nanowire with a magnet and demonstration of force detection based on electron spin resonance (ESR) were performed.

One of the most important issues for sophistication is the force sensitivity and resolution of cantilever probes in MRFM. The force sensitivity may be systematically improved by fabricating cantilevers with (1) softening to reduce the spring constant, (2) weight lighting to increase the resonance frequency and (3) miniaturization to reduce the viscous drag from the environment and increase the Q factor, then equipping the magnet with (4) stronger magnetic field gradients and operating it at (5) low temperatures. Then, It have considered the minimum detectable force because the smallest force that can be detected by observing the deflection of a cantilever is limited by thermomechanical noise.

According to this equation of thermomechanical noise, it is found that a high Q factor, thin, narrow, and long probe structure such as a nanowire is desirable for detecting small force. It is found that the force sensitivity of 100 aN can be obtained in more than 20 kHz of resonant frequency with the spring constant below 10^{-2} N/m (Assumed 200 nm thickness and thickness, $Q = 100000$, $T = 293$ K). A mirror and a magnet support part is required to the real design of the nanowire probe at current MRFM device. The length from 30 μm to 92 μm of the nanowire probe with a mirror can achieve 100 aN or less of force sensitivity. We can also design for silicon nanowire with two types of magnets: a Ni thin film magnet and a Nd-Fe-B particle magnet. A smaller size of the magnet has higher magnetic field gradient, and force sensitivity is also higher. However, the size of magnet should be optimized according to a sample size because short distance of resonant slice which generated by the small magnet is limited to the detectable depth of the sample.

Silicon nanowire probes were fabricated by top-down process using silicon on insulator wafers having top silicon thicknesses of 100 nm and 200 nm. The width and length of the fabricated nanowires are 160 nm ~ 220 nm and 32 μm ~ 72 μm and the octagon mirror with 5 μm of the inradius is formed at the middle of the probe. Two different types (thin film and particle) of magnets are integrated at the end of the probe. The magnet formation on the nanowire probe is difficult to fix the magnet at the end of the nanowire. In this research, it is found that the magnet support part is required to fix the nickel magnet film at the end of nanowire design. Furthermore, the nanowire probe with the nickel magnet cannot be annealed to increase the Q factor because of nickel silicide formation. We have concluded that the nickel magnet is not suitable choice as a magnet material on nanowire probes of MRFM, which requires a high Q factor to detect small force. In order to increase the reflectivity for fine measurement of interferometer in MRFM system, the tungsten films is partially deposited on the silicon mirror. Since the intensity of interferogram should be increased with the metalized mirror, the deflection signal using the interferometer in MRFM system might be improved with lower noise level. Instead of the nickel magnet on the nanowire probe, a Nd-Fe-B magnet is putted on the end of probe using a manipulator. The anneal process has been successfully done, and the Q factor is increased as expected. To achieve ideal increment of Q factor by annealing, the mounting process of the magnet particles need to be optimized to avoid any contamination to the silicon nanowire probes.

As the first step of the characterization of the silicon nanowire probe, the resonance responses of three different lengths of nanowire probe with 32 μm, 52 μm and 72 μm were measured. The different resonant frequency and Q factor of the nanowire probes are observed. Both of values are decreased as their length increased. The force sensitivity is improved when the length of the probe is longer. When the Ni magnet is integrated on the silicon nanowire probe, the resonant frequency and the Q factor are decreased. Therefore, the force sensitivity became reduced from 5.3 times to 6.5 times by integrated nickel. Using the nickel thin film as a magnet for MRFM, there are two problems. The first issue is the difficulty to perform annealing process because nickel-silicide is formed by the reaction between nickel and silicon over 300°C. The second issue is that the resonance slice is generated in a very short distance from the magnet. Thus, it is limited to measurable depth of sample.

With the Nd-Fe-B magnet, however, the force sensitivity with decreasing the resonant frequency and the Q factor are decreased from 87 $aN/Hz^{1/2}$ to 240 $aN/Hz^{1/2}$ about 2.7 times. Since the silicon nanowire probe with Nd-Fe-B magnet can be annealed and the magnet can be magnetized after the annealing process, the reduced Q factor can be restored by the post anneal process. Additionally, the generated resonance slice in MRFM measurement is forming at a sufficient distance to measure the samples with micron size. The Nd-Fe-B particle magnet is the most suitable material as the magnet on the nanowire probe instead of the Ni thin film magnet.

In order to obtain MRFM signals, the fabricated silicon nanowire probe has been installed in MRFM device. A scanning measurement of force map based on ESR for three-dimensional imaging of radicals has been demonstrated using the fabricated nanowire probe.

The force signal can be measured by the silicon nanowire probe with the Ni thin film magnet. Detected force is $1.3 \times 10^{-15}\ N/\sqrt{\mathrm{Hz}}$ and force noise appears on even another part from slice with magnitude of $2.6\times10^{-16} N/\sqrt{\mathrm{Hz}}$. Then, S/N ratio that is calculated in MRFM signal, is 5.

The experimental result of F_{min} using the fabricated probe with the Nd-Fe-B magnet is 82 aN/√Hz. The calculated spin density at the peak of 1.9 GHz is 4.6×10^{18} spins/cm^3. The estimated spin density: 1.5×10^{21} spins/cm^3. Calculated result is about 10^3 spins smaller than the standard value. This reduction of spins is possibly due to oxidation reaction with long-term air exposure. Typical three-dimensional MRFM data can demonstrating a sequence of two-dimensional scans from the magnet to a particle sample distances in 2 μm steps.

In order to evaluate the defects or radical distribution subsurface in the sample without destroying, thin film measurement system is also required. The method that lengthens the distance between the magnet and the mirror from 10 μm to 50 μm so that measurable area can be larger, for designing the probe the estimated thickness of the resonant slice is 220 nm and the calculated spin density is 4.1×10^{18} spins/cm^{3}at the peak. With only lengthening distance between the magnet and the mirror, it is possible to measure MRFM signal of thin film for certain area.

As the result, the Si nanowire probes have a high potential ability as a force sensor using in various instruments at room temperature. Fabricating the Si nanowire probes with magnet is expected to provide a high force resolution and response speed for force sensing and nanometric imaging, such as MRFM detection.

論文審査結果の要旨

半導体微細加工技術をベースにしたマイクロ・ナノマシニング技術を用いると，機械要素を小型化して高感度なセンサが実現できる。近年，振動子の最少加工寸法をナノスケールまで小さくすることで，より高感度な力センサを実現する研究が進められている。この力センサの一つの応用は，磁気共鳴を検出し，試料中の各種磁気スピンの密度分布をナノスケールの分解能で観測する顕微鏡である。この顕微鏡は磁気共鳴力顕微鏡と呼ばれ，磁気共鳴が起きた際の振動子の先端に形成した磁石と試料中の磁気スピンとの間に働く力の変化からスピンを検出してスピン密度情報を得ることができる。従来の磁気共鳴力顕微鏡用プローブは，熱機械ノイズを低減するために極低温に冷却する必要があり，測定装置が複雑になりその応用には制限がある。本論文では，室温でも高感度なセンシングを可能にするために，ナノ細線型のプローブを開発している。また，ナノ細線型のプローブを用いて，室温でアトニュートン(aN)オーダーの力分解能を達成し，試料中のラジカル密度の測定に成功している。本論文は，これらの研究成果をまとめたものであり，全編 5 章からなる。

第 1 章は緒言であり，本研究の背景や目的について述べている。

第 2 章では，磁気共鳴力顕微鏡プローブの設計論について述べている。プローブを用いた検出可能な最少の力は，熱機械ノイズによって制限されており，その共振周波数やばね定数，Q 値などによって決まる。検出可能最少力のスケーリングについて考察し，プローブの寸法と検出可能最少力の関係について論じている。この結果として，プローブの構造が細く，長いナノ細線型の構造が検出可能最少力の点で有利であることを見出している。これは，高感度な磁気共鳴力プローブを実現するための重要な知見である。

第 3 章では，磁気共鳴力顕微鏡プローブの作製方法について述べている。電子ビームリソグラフィーを用いたトップダウン技術により，先端に磁石をもつシリコンプローブの作製に成功している。このような極めて高感度なナノ細線構造をもつプローブの作製方法を開発していることは重要な成果である。また，作製したプローブを水素雰囲気中で熱処理してその機械的な Q 値を増加させることに成功している。これは，プローブの高感度化のための重要な成果である。

第 4 章では，作製したプローブを用いて室温で電子スピンの磁気共鳴信号の検出に成功している。試料としてラジカルを含んだ数ミクロン程度の大きさの有機物を用い，2 次元の力マップの取得に成功している。また，RF 励起信号の周波数と共鳴信号が起きる位置の関係から磁場勾配を算出し，この値を基に試料中のラジカル密度の計測ができることを実証している。さらに，薄膜形状の試料においても同様に 2 次元信号を取得して試料中のラジカル密度を算出している。試料とプローブの距離を変化させて同様の信号を得ることで，3 次元情報に対応した信号を得ることにも成功している。得られた実際の信号ノイズから，プローブの検出可能最少力が周波数当たり 82aN であり，さらにプローブはサブミクロンの空間分解能をもつことが示されている。このように開発したナノ細線プローブが室温でも優れた感度や空間分解能を持つことを示しているのは重要な成果である。

第 5 章は結論である。

以上要する本論文は，室温においても高感度に磁気共鳴を利用してマイクロサイズの試料中の磁気スピンの密度分布を測定することができるナノ細線型の磁気共鳴力顕微鏡プローブを開発して重要な成果を得たものであり，機械システムデザイン工学およびナノ機械工学の発展に寄与するところが少なくない。

よって，本論文は博士(工学)の学位論文として合格と認める。